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COMMUNICATION

An improved process for the surface modification of SiO_2 nanoparticles†

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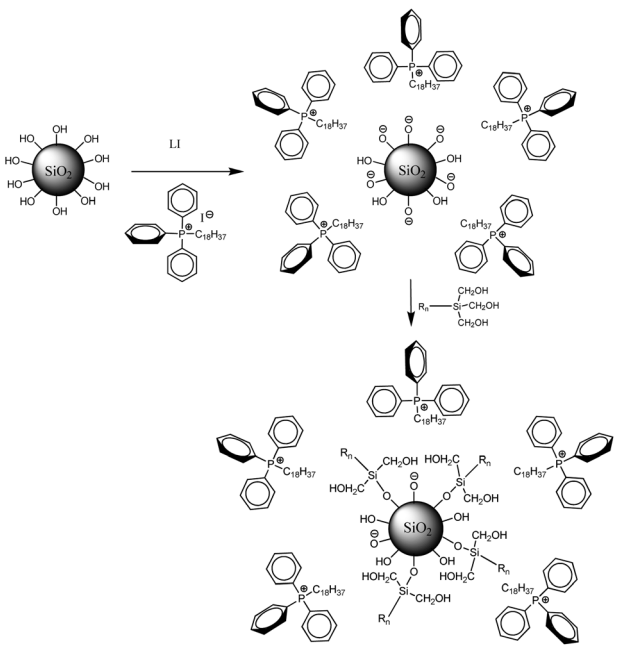
A phosphonium ionic liquid is used as an activator of silanol groups to improve the surface functionalization of silica nanoparticles with fluorosilanes in supercritical CO_2.

Due to their excellent optical, electrical and mechanical properties as well as their unique advantages such as high surface area, nanoparticles can play a key role in many nanotechnology applications.[1,2] For example, significant R&D resources have been devoted to nanoparticle technology in diverse fields including electronic and biomedical devices, automotive parts, coatings, drug delivery, gene delivery, catalysis and polymers.[3–14] For several of these applications surface functionalization is an important requirement. For example, to change the polarity of the nanoparticles and promote dispersion in organic solvents or polymers chemical treatment by cation exchange or grafting using organosilanes has been extensively practiced.[15–17] In addition, surface functionalization has been used to improve the stability of the nanoparticles and avoid aggregation in various media.[18,19]

Surface functionalization is typically carried out in the presence of organic solvents. In some instances and to make the process greener, supercritical CO_2 ($scCO_2$) has been used in place of conventional solvents. However, the grafting density tends to be relatively low. It has been reported that small amounts of a highly basic ionic liquid (<0.5 wt%) can generate silanoates on the surface of silica. We combine here the use of an ionic liquid in $scCO_2$ to increase the grafting density of fluorosilane on silica. The process results in doubling of the grafting densities with the resulting nanoparticles exhibiting CO_2-philic behavior. In addition to the increased reactivity and higher grafting density the new process offers the following additional advantages: (i) this is a one-step process, (ii) the use of organic solvents is completely eliminated, (iii) the lengthy steps of purification and drying of the silica are replaced by dilution and filtration, (iv) the ionic liquid can be recovered and reused. We note that our process differs from previous reports using $scCO_2$ in that low pressures (80 instead of 400 bar) and less amounts of silane (only 10 wt% compared to a 3–10 times molar excess of the corresponding coupling agents used in the literature) are required.[20,21] In addition, previous reports utilizing $scCO_2$ were limited to dry, fumed silica instead of aqueous dispersions used in our approach. While the primary particles of fumed silica are small and comparable to that of colloidal silica, drying tends to lead to particle agglomeration.

While the method can be applicable to different oxides we demonstrate it here using colloidal silica and three different fluorosilanes: (i) perfluorooctyl-methyldimethoxysilane (DMS), (ii) perfluorooctyl-trichlorosilane (TCS), and (iii) perfluorooctyl-triethoxysilane (TES). Triphenyloctadecyltriphenylphosphonium iodide ($C_{18}P\ I^-$) was used as the surface activator. The synthesis of fluorinated-functionalized silicas is presented in Scheme 1. The synthesis and characterization of the IL have been reported in a previous publication.[22]

To prepare the new fluorosilane modified nanoparticles the fluorosilanes were reacted with a suspension of commercial, colloidal silica (30 wt%) in the presence of $C_{18}P\ I^-$.



Scheme 1 Schematic of nanoparticle modification in the presence of the ionic liquid.

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†Electronic supplementary information (ESI) available: Synthesis procedure, ^{1}H-NMR, ^{13}C-NMR spectra and characterization data (TGA, DSC) for IL $C_{18}P\ I^-$. Schematic for $scCO_2$ system synthesis. See DOI: 10.1039/c2gc36369k

Specifically 100 mL of the 30 wt% colloidal suspension (Ludox HS-30) with the appropriate amount of the chosen fluorinated reagent (10 wt% of silica) and 0.2 wt% of $C_{18}P\ I^-$ were added into a 300 mL high pressure reactor. CO_2 was added until the pressure reached 60 bar at 25 °C. Then the reaction chamber was heated to 80 °C. After 3 h of reaction, the autoclave was depressurized at a rate of 3.6 bar per second. The product was redispersed in distilled water (50 mL) using first a high shear mixer (5 min at 4000 rpm min^{-1}) followed by ultrasonification (2 min, 2 times) and again with the high shear mixer (5 min at 4000 rpm min^{-1}). Then, the suspension was filtered to recover the product as well as the ionic liquid, which is a liquid at 85 °C but crystallizes below 75 °C (DSC curve in the ESI†). For comparison the reaction was also run under identical conditions but in the absence of the ionic liquid.

Thermogravimetric analysis (TGA)‡ traces for the products prepared with and without the IL are presented in Fig. 1 and 2.

First, we note the high thermal stability of the modified nanoparticles where, besides a weight loss at low temperature most likely corresponding to small amounts of remaining solvent, the decomposition of the organic groups on the surface commences at temperatures above 350 °C. The weight loss between 350 and 700 °C is due to the decomposition of the chemically-bonded fluorinated ligands and thus it corresponds to the amount of reacted groups on the silica surface. The weight loss data (and the corresponding grafting density, d, calculated from $d = \Delta w/M_f$, where Δw is the weight loss and M_f is the molecular weight of the fluorinated silanes) for all samples are summarized in Table 1. First we compare the amount of fluorosilane reacted with silica in the absence of IL. The trifunctional alkoxy and dialkoxy silane lead to lower weight loss and grafting density (0.06–0.08) compared to the trichlorosilane, where the highest surface coverage was obtained (0.15). These differences are consistent with earlier reports in the literature.[23,24] For example, Engelhardt *et al.* showed that multifunctional chlorosilanes have better reactivity than alkoxysilanes consistent with our results. Others have noted that the reactivity of alkoxysilanols with surface silanols increases with the decreasing number of OH groups present on the coupling agent.[25,26]

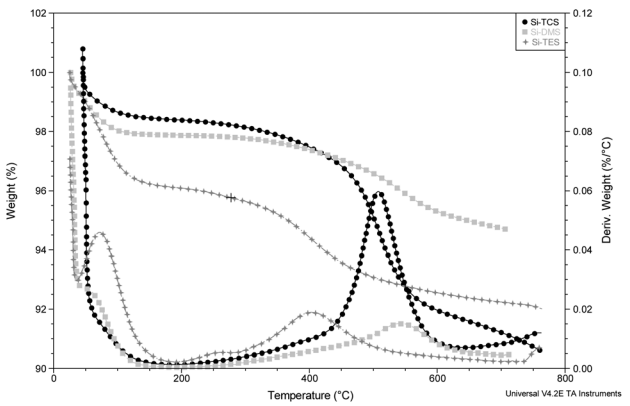

Fig. 1 Weight loss and weight loss derivative as a function of temperature for systems prepared in the absence of IL for (●) SiO_2–TCS, (■) SiO_2–DMS, (+) SiO_2–TES (heating rate: 20 K min^{-1}, nitrogen atmosphere).

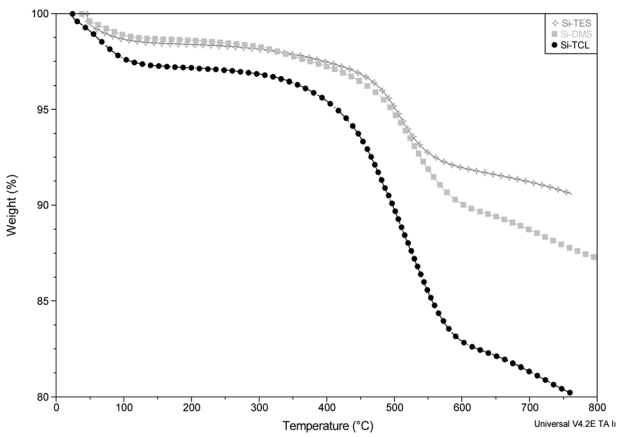

Fig. 2 Weight loss and weight loss derivative as a function of temperature for systems prepared in the presence of IL (TGA, DTG) of the (●) SiO_2–TCS, (■) SiO_2–DMS, (+) SiO_2–TES (heating rate: 20 K min^{-1}, nitrogen atmosphere).

Table 1 Characterization of the fluorinated groups on silica as determined by TGA

Samples	Weight loss (%)	Graft density d (mmol g^{-1})	No. of groups X (per nm^2)	Yields (%)
Si–TES without IL	3	0.06	0.164	7
Si–DMS without IL	3.5	0.08	0.219	9
Si–TCL without IL	7.3	0.15	0.413	17
Si–TES with IL	10	0.22	0.610	24
Si–DMS with IL	10	0.22	0.610	24
Si–TCL with IL	15	0.31	0.850	34

The presence of the IL significantly improves the grafting density of all fluorosilanes on the silica nanoparticles. In fact, the grafting density increases by at least a factor of 2 and by as much as 3.6 for TCL and TES, respectively. We attribute this significant improvement in the grafting density to the basicity of the phosphonium ionic liquid that generates silanoate groups on the silica surface with the phosphonium ions acting as the counter cations (Scheme 1).[27] Similar trends were noted by Lungwitz *et al.* on phosphonium and imidazolium ionic liquids in their work to develop new materials for heterogeneous catalysis.[26]

The number of groups on the surface, X, can be calculated using $X = dA/S$ where d is the grafting density, A the Avogadro number, and S the surface area.[20] If we assume an average number of 2.5 SiOH/nm^2,[28,29] the functionalization yield (extent of functionalization) in the presence of the IL was 24–34% compared to 7–17 for the controls (*i.e.* in the absence of the IL) (Table 1).

The stability of the functionalized nanoparticles and their morphology were investigated by transmission electron microscopy (TEM) and by dynamic light scattering (DLS) analysis. Fig. 3 shows TEM images of TES treated silica. The size of the nanoparticles was measured using Image J Software analysis developed by the U.S. National Institutes of Health.

Regardless of the fluorosilane used a morphology composed of well-separated silica nanoparticles is observed. The image analysis for the treated nanoparticles reveals an average diameter of about 13.5 ± 2 nm compared to 12 ± 2 nm for the unmodified

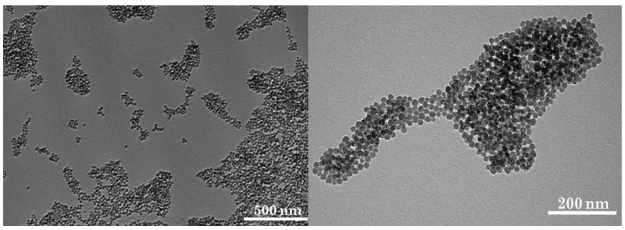

Fig. 3 TEM micrographs of Si–TES.

silica. The slight increase is attributed to the size of the grafted fluorosilane chains. Dynamic light scattering (DLS) analysis was also used to complement the TEM results. A particle size of 25 nm, 28 nm and 30 nm was obtained for Si–TES, Si–DMS and Si–TCL, respectively. Based on the average diameter obtained by transmission electron microscopy, we can conclude that the aggregates formed are composed of 2 to 3 particles of silica. We note that the slight agglomeration in water is consistent with the fluorinated silica being CO_2-philic and not well dispersible in water.[30,31]

To demonstrate that the method is applicable to other oxides beyond silica a suspension of alumina was reacted with perfluorooctyl triethoxysilane (TES) as a coupling agent in the presence of the ionic liquid. Thermogravimetric analysis shows a weight loss of 10%, which is equal to the weight loss (and thus grafting density) of the silica nanoparticles. In addition, the ^{29}Si NMR spectrum shows a peak at −52 ppm corresponding to a T2 species and confirming the presence of Al–O–Si bonds.[32] These results highlight that the process can be extended to different oxide nanoparticles provided they are endowed with surface hydroxyl groups.

In conclusion, we have developed a new, "green" surface modification of colloidal silica nanoparticles with fluorosilanes. The use of a basic IL in $scCO_2$ as an activator improves the extent of functionalization by a factor of 2–3.6 depending on the fluorosilane by generating silanoate groups on the silica surface. Moreover, the resulting treatment changes the surface characteristics of the silica nanoparticles from hydrophilic to CO_2-philic.

Acknowledgements

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Notes and references

‡ *Thermogravimetric analyses (TGA)* were performed using a Q500 thermogravimetric analyser (TA Instruments). The samples were heated to 700 °C at a rate of 20 K min^{-1} under a nitrogen flow of 90 mL min^{-1}.

Transmission electron microscopy (TEM) was performed at the Center of Microstructures (Université de Lyon) using a Philips CM 120 field emission scanning electron microscope with an accelerating voltage of 80 kV. The samples were prepared at room temperature and were set on copper grids for observation.

Differential scanning calorimetry (DSC) analyses were performed on a Q20 (TA Instruments) between −80 °C and 200 °C for IL. The samples were heated or cooled at a rate of 10 K min^{-1} under nitrogen flow.

Size and size distribution were measured by *dynamic laser light scattering* on a Zetasizer NanoZS (Malvern Instruments) and the *z*-average diameter was calculated from the correlation function according to the cumulant method. The samples were diluted in pure distilled water. The dilution was optimized for each sample, in order to have an accurate signal to noise ratio.

The silica used in this work is Ludox® HS-30 (30 wt% in water) with a specific area of 220 m^2 g^{-1} and it was provided by Sigma Aldrich. 1*H*,1*H*,2*H*,2*H*-perfluorooctyltriethoxysilane, 1*H*,1*H*,2*H*,2*H*-perfluoromethyldimethoxysilane were purchased from Lancaster, and 1*H*,1*H*,2*H*,2*H*-perfluorooctyltrichlorosilane was obtained from Gelest.

1 P. T. Anastas, *Handbook of Green Chemistry: Green Solvents*, Wiley-VCH, 2010.
2 P. T. Anastas, *Handbook of Green Chemistry: Green Processes*, Wiley-VCH, 2012.
3 R. Saidur, K. Y. Leong and H. A. Mohammad, *Renewable Sustainable Energy Rev.*, 2011, **15**, 1646.
4 G. A. Pilkington and W. H. briscoe, *Adv. Colloid Interface Sci.*, 2012, **179**, 68.
5 K. V. Wong and O. De Leon, *Adv. Mech. Eng.*, 2010, **2010**, 1.
6 S. P. Jang and S. Choi, *Appl. Therm. Eng.*, 2006, **19**, 432.
7 M. Kole and T. K. Dey, *Exp. Therm. Fluid Sci.*, 2010, **34**, 677.
8 I. Sondi and B. Salopek-Sondi, *J. Colloid Interface Sci.*, 2004, **275**, 177.
9 P. Yang, S. Gai and J. Lin, *Chem. Soc. Rev.*, 2012, **41**, 3679.
10 P. J. Hotchkiss, S. C. Jones, S. A. Paniagua, A. Sharma, B. Kippelen, N. R. Armstrong and S. R. Marder, *Acc. Chem. Res.*, 2012, **45**, 337.
11 S. Behrens, *Nanoscale*, 2011, **3**, 877.
12 J. E. Lee, N. Lee, T. Kim, J. Kim and T. Hyeon, *Acc. Chem. Res.*, 2011, **44**, 893.
13 F. M. Kievit and M. Zhang, *Acc. Chem. Res.*, 2011, **44**, 853.
14 R. Hao, R. Xing, Z. Xu, Y. Hou, S. Gao and S. Sun, *Adv. Mater.*, 2010, **22**, 2729.
15 F. Avalos, J. C. Ortiz, R. Zitzumbo, M. A. López-Manchado, R. Verdejo and M. Arroyo, *Appl. Clay Sci.*, 2009, **43**, 27.
16 H. A. Patel, R. S. Somani, H. C. Bajaj and R. V. Jasra, *Appl. Clay Sci.*, 2007, **35**, 194.
17 E. P. Giannelis, *Adv. Mater.*, 1996, **8**, 29.
18 D. J. Shaw, *Introduction to Colloid and Surface Chemistry*, Butterworth-Heinemann, Oxford, UK, 1991.
19 D. Quemada and C. Berli, Energy of interaction in colloids and its implication in rheological modelling, *Adv. Colloid Interface Sci.*, 2002, **98**, 51.
20 P. M. Visintin, R. G. Carbonell, C. K. Schauer and J. M. Desimone, *Langmuir*, 2005, **21**, 4816.
21 N. M. Scully, L. O. Healy, T. O. Mahony, J. D. Glennon, B. Dietrich and K. Albert, *J. Chromatogr., A*, 2008, **99**, 1191.
22 S. Livi, J. Duchet-Rumeau and J. F. Gerard, *Chem. Commun.*, 2011, **47**, 3589.
23 D. W. Sindorf and G. E. Maciel, *J. Am. Chem. Soc.*, 1983, **105**, 3767.
24 H. Engelhardt and P. Orth, *J. Liq. Chromatogr.*, 1987, **10**, 1999.
25 L. D. White and C. P. Tripp, *J. Colloid Interface Sci.*, 2000, **224**, 417.
26 C. P. Tripp and M. L. Hair, *Langmuir*, 1995, **11**, 149.
27 R. Lungwitz, T. Linder, J. Sundermeyer, I. Tkatchenko and S. Spange, *Chem. Commun.*, 2010, **46**, 5903.
28 M. K. Kidder and A. C. Buchanan III, *J. Phys. Chem. C*, 2008, **111**, 3027.
29 M. S. Wong, H. C. Huang and J. Y. Ying, *Chem. Mater.*, 2002, **14**, 1961.
30 M. Z. Yates, P. S. Shah, K. P. Johnston, K. T. Lim and S. Weber, *J. Colloid Interface Sci.*, 2000, **227**, 176.
31 L. Calvo, J. D. Holmes, M. Z. Yates and K. P. Johnston, *J. Supercrit. Fluids*, 2000, **16**, 247.
32 D. Yang, B. Paul, W. Xu, Y. Yuan, E. Liu, X. Ke, C. Guo, Y. Xu, Y. Sun and H. Zhu, *Water Res.*, 2010, **44**, 741.